

# (12) UK Patent Application (19) GB (11) 2 301 372 (13) A

(43) Date of A Publication 04.12.1996

(21) Application No 9609495.8	(51) INT CL <sup>6</sup> C09K 11/64
(22) Date of Filing 07.05.1996	
(30) Priority Data (31) 07130609 (32) 29.05.1995 (33) JP 08052968 11.03.1996	(52) UK CL (Edition O ) C4S S33Y S43Y S561 S59Y S60X S60Y S602 S62X S621 S625 S66Y S671 S70Y S705 S708 S709 S71Y S712 S714 S715 S717 S720 S723 S725 S73Y S732 S735 S738 S739 S740 S741 S751 S753 S756 S757 S758 S759 S76Y S760 S763 S764 S765 S766 S767 S768 S769 S770 S771 S78Y S781 S782 U1S S1411 S1927 S1928 S3077
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(54) Afterglow lamp comprising a long decay phosphor containing activated europium oxide

(57) An afterglow lamp comprises:

(i) a light emitting section for the conversion of electrical energy to optical energy;  
(ii) a fluorescent layer, excited to emit light by the light emitting section, comprising a long decay phosphor having the general formula:  
$$[M(1-p-q)Eu(p)Q(g)]O.n[Al(1-m)B(m)]2O3.kP2O5.aX$$
wherein: p and q are from 0.0001 to 0.5;  
n is from 0.5 to 3.0;  
m and a are from 0 to 0.5;  
k is from 0 to 0.2;  
a : n is from 0 to 0.4;  
M is at least one of Mg, Ca, Sr, Ba and Zn;  
Q is a coactivator selected from at least one of Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu;  
X is at least one of F, Cl, Br and I.

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FIG. 1

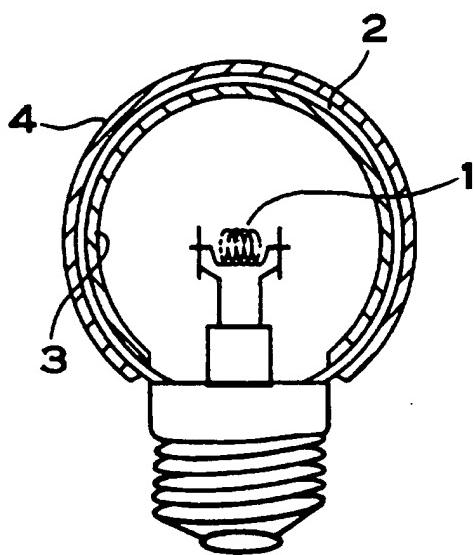
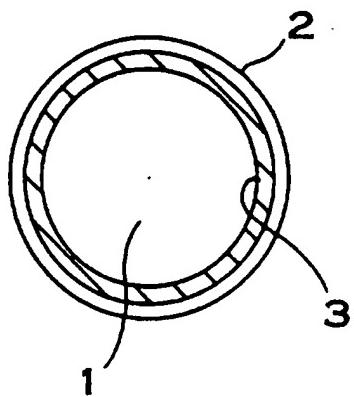


FIG. 2



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FIG. 3

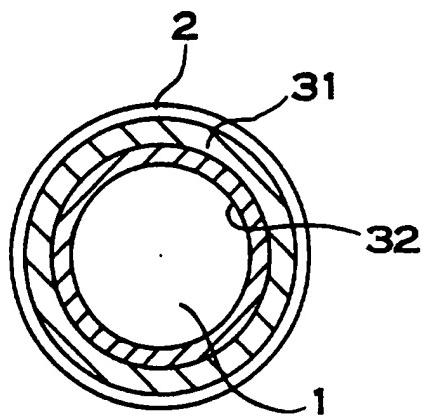
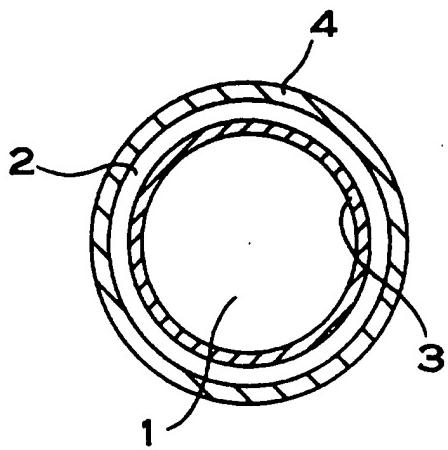


FIG. 4



**2301372**

**TITLE OF THE INVENTION**

**AFTERGROW LAMP**

**BACKGROUND OF THE INVENTION**

The present invention relates to an aftergrow lamp, the inner surface of which is coated with a boroaluminate long decay phosphor of a specified composition having aftergrow characteristics.

An enforcement ordinance of the Fire Service Act, the Fire Prevention Regulations of each city or the like obliges people to equip guide lamps in places where many people gather such as theaters and hotels. When usual electric sources are cut on account of an earthquake, a fire or other disasters, it is necessary that reserve electric sources are automatically put on to light such guide lamps for more than 20 minutes. However, if the reserve electric sources are also cut or feeding circuits are cut on account of the disaster, the guide lamps are cut off. In such cases, a complicated underground market, a long tunnel, a multistory building at night and the like become very dangerous places. Further, since the conventional guide lamps are of complicated structure, it takes much time and high cost to equip the same. Therefore, such guide lamps are rarely equipped except the places where the Laws oblige to equip the same.

Further, guide lamps are required not only in such an emergency as abovementioned. If almost all buildings including large building such as company buildings, department stores, school houses and factories, and stores and houses are equipped with guide lamps of simple structure and low cost which allow the users to see their feet from the time when they put off switches of lights of a room, corridor or staircase till they reach the exit, they can spend more safe and comfortable lives.

In this connection, an art of providing a light storing substance capable of absorbing and storing optical energy emitted from a light source on a supporting member such as a shade positioned in a place where the light from the light source reaches has been disclosed in Japanese Non-examined Patent Publication No.58-121088 issued July 19,1983. By using this light storing substance, it becomes unnecessary to provide reserve electric sources. However, the conventional light storing substances are disadvantageous in that they are chemically unstable and apt to be deteriorated by ultraviolet rays, high temperatures, moisture or the like. Further, the aftergrow of these light storing substances are dark and short. Furthermore, sufficient light cannot be obtained according to the method of coating a supporting member with a light storing substance.

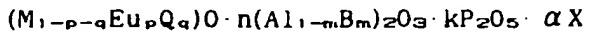
#### SUMMARY OF THE INVENTION

An object of the present invention is to provide a guide lamp which enables the users to use a long and light aftergrow, and requires neither any reserve electric source even in an emergency nor any special illuminator, for example, one coated with a light storing substance.

The inventor, after studies, has found that the abovementioned object can be realized by coating the inner or outer surface of a guide lamp with an aluminate fluorescent substance of a specified composition, and has completed the invention.

An aftergrow lamp according to the present invention comprises a light emitting section for converting electric energy into optical energy, and a light transmittable glass for covering the light emitting section. A fluorescent substance layer is provided on at least one of the inner surface and the outer surface of the light transmittable glass.

The fluorescent substance layer is characterized by comprising a long decay phosphor represented by the general formula:



in which the values of p, q, n, m, k,  $\alpha$ , and  $\alpha/n$  are in the ranges:

$$0.0001 \leq p \leq 0.5$$

$$0.0001 \leq q \leq 0.5$$

$$0.5 \leq n \leq 3.0$$

$$0 \leq m \leq 0.5$$

$$0 \leq k \leq 0.2$$

$$0 \leq \alpha \leq 0.5$$

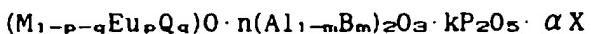
$$0 \leq \alpha/n \leq 0.4$$

M is at least one selected from a group of divalent metals consisting of Mg, Ca, Sr, Ba and Zn;

Q is a coactivator which is at least one selected from a group consisting of Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; and

X is at least one selected from a group of halogen elements consisting of F, Cl, Br and I.

By further controlling the abovementioned composition in the following specified ranges, the fluorescent color and the aftergrow color can be selected. In order to prepare a green light emitting long decay phosphors having the light emission peak wavelength near 520nm, the following composition range is selected. This is a boroaluminate fluorescent substance activated by a divalent europium, a long decay phosphor is selected which is represented by the following chemical composition formula in the following composition range and the main component of the crystalline structure of which is a monoclinic system:



$$0.0001 \leq p \leq 0.5$$

$$0.0001 \leq q \leq 0.5$$

$$0.5 \leq n < 1.5$$

$$0.0001 \leq m \leq 0.5$$

$$0 \leq k \leq 0.2$$

$$0 \leq \alpha \leq 0.5$$

$$0 \leq \alpha/n \leq 0.4$$

in which more than 70 mol% of M is Sr.

In order to prepare a blue light emitting aftergrow fluorescent substance having the light emission peak wavelength near 440nm, the following composition range is selected. Thus, in a boroaluminate fluorescent substance activated by a divalent europium, a long decay phosphor is selected which is represented by the following chemical composition formula in the following composition range and the main component of the crystalline structure of which is a monoclinic system:



$$0.0001 \leq p \leq 0.5$$

$$0.0001 \leq q \leq 0.5$$

$$0.5 \leq n < 1.5$$

$$0.0001 \leq m \leq 0.5$$

$$0 \leq k \leq 0.2$$

$$0 \leq \alpha \leq 0.5$$

$$0 \leq \alpha/n \leq 0.4$$

in which more than 70 mol% of M is Ca.

In order to prepare blue green light emitting aftergrow fluorescent substance having the light emission peak wavelength near 490nm, the following composition range is selected. Thus, in a boroaluminate fluorescent substance activated by a divalent europium, a long decay phosphor is selected which is represented by the following chemical composition range and the main component of the crystalline structure of which is a rhombic system:



$$0.0001 \leq p \leq 0.5$$

$$0.0001 \leq q \leq 0.5$$

$$1.5 \leq n \leq 3.0$$

$$0.0001 \leq m \leq 0.5$$

$$0 \leq k \leq 0.2$$

$$0 \leq \alpha \leq 0.5$$

$$0 \leq \alpha/n \leq 0.4$$

in which 70 mol% M is Sr.

This fluorescent substance the main component of the crystalline structure of which is a rhombic system is excellent especially in heat resistance. Therefore, if this fluorescent substance is used for a fluorescent lamp requiring a step of heating the fluorescent substance, it is advantageous that lowerings of the light emitting brightness degree and the aftergrow brightness degree thereof can be reduced.

In order to prepare a blue green light emitting long decay phosphor having the light emission peak wavelength near 490nm, selecting the following composition range is especially preferable in respects of the light emitting brightness degree, the aftergrow brightness degree and the heat resistance. Thus, in a boroaluminate fluorescent substance, activated by a divalent europium a long decay phosphor is selected which is represented by the following chemical composition formula in the following composition range and the main component of the crystalline structure of which is a rhombic system:



$$0.0001 \leq p \leq 0.5$$

$$0.0001 \leq q \leq 0.5$$

$$1.7 \leq n \leq 2.0$$

$$0.0001 \leq m \leq 0.5$$

$$0 \leq k \leq 0.2$$

$$0 \leq \alpha \leq 0.5$$

$$0 \leq \alpha/n \leq 0.4$$

in which M is Sr.

A aftergrow lamp according to the present invention can provide a long and bright aftergrow without using any emergency reserve electric source.

Especially when a blue green light emitting long decay phosphor of the crystalline structure of which is a rhombic system is selected, the aftergrow brightness degree thereof becomes remarkably high, and further, since the water resistance of the fluorescent substance are also improved, it can be applied to a lamp in which the long decay phosphor is in direct contact with the outer air.

It is very economical to apply this aftergrow fluorescent lamp to a guide lamp, because the conventional illuminating lamp can be used as it is without providing any special illuminating lamp, for example, one coated with a light storing substance. As a result, cost used for choosing the places where the guide lamps are provided can be decreased.

Further, when this aftergrow fluorescent lamp is incorporated in a conventional guide lamp provided with reserve electric source and used, it ensures a very reliable guide lamp since it can function as a guide lamp even if the reserve electric source or the feeding circuit is cut in an emergency.

In addition, this aftergrow fluorescent lamp can be used not only as an emergency guide lamp equipped in a room, corridor or staircase for illuminating one's feet after he switched off the main light till he reaches an exit, because this aftergrow lamp can provide an aftergrow of a high brightness degree even after the switch is cut.

The above and further object and features of the present invention will more fully be apparent from the following detailed description given with accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig .1 is a sectional view of an aftergrow lamp according to the present invention.

Fig. 2 is a sectional view of an aftergrow lamp according to the present invention.

Fig. 3 is a sectional view of an aftergrow lamp according to the present invention.

Fig. 4 is a sectional view of an aftergrow lamp according to the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

An aftergrow lamp is coated with long decay phosphors. In this aftergrow lamp, the long decay phosphor is designed to receive the light emitted from the lamp. The long decay phosphor is excited by the light emitted from the lamp and emits aftergrow light. The light of the lamp capable of exciting the long decay phosphor vary according to the chemical composition of the long decay phosphor as abovementioned.

The long decay phosphor of the present invention can be many kinds of lamps. The long decay phosphor of the present invention can be applied all kinds of lamps now in practical use such as incandescent lamps, fluorescent lamps, HID lamps and halogen lamps. An aftergrow lamp of the present invention can be obtained by coating the long decay phosphor on the inner surface and/or outer surface of a light transmittable glass covering a light emitting section 1 of the lamp and thereby forming an inner fluorescent layer 3 and/or the outer fluorescent layer 4 as shown in Fig.1.

The thickness of the long decay phosphor layer varies according to the particle size of the long decay phosphor used, but 5 to 100  $\mu\text{m}$  is

preferable. If the thickness of the long decay phosphor layer is smaller than this range, the amount of the applied long decay phosphor is too small, aftergrow can hardly be provided. When the thickness is larger than this range on the contrary, the light emitted from the lamp is intercepted by the long decay phosphor, and the original function of the lamp as an illuminator is lowered.

All the aftergrow lamps according to the present invention are designed as abovementioned. However, especially in a fluorescent lamp, the fluorescent substance of the fluorescent layer on the inner surface of the glass tube is excited by ultraviolet rays and emits light. Therefore, this ultraviolet rays can be directly utilized. When the long decay phosphor is applied on the inner surface of the glass tube of a fluorescent lamp, the long decay phosphor is directly excited also by 253.7nm mercury rays radiated from a positive column which is a light emitting section of the fluorescent lamp. Consequently, an aftergrow fluorescent lamp can be obtained by applying only the long decay phosphor on the fluorescent lamp. In this case, the aftergrow becomes extremely bright. However, since the lamp is usually used as a usual white light fluorescent lamp, preferably the long decay phosphor is used in combination with a fluorescent substance for a fluorescent lamp so that the long decay phosphor can receive the light of the fluorescent substance for the fluorescent lamp and thereby emit aftergrow

An embodiment of an aftergrow fluorescent lamp according to the present invention in which the long decay phosphor receives light of another fluorescent substance will now be explained with reference to a sectional view of Fig. 2 in which a fluorescent lamp is sectioned perpendicularly to the longitudinal direction of its tube. A fluorescent substance layer 3 formed on the inner surface of a light transmittable glass 2 is excited by optical energy (ultraviolet ray radiating energy)

converted from electric energy mainly in the light emitting section 1 of a positive column. In this case, the long decay phosphor and the illuminating fluorescent substance capable of exciting the long decay phosphor may be mixed in the fluorescent layer, and this method is most easily carried out.

Further, as shown in a sectional view of a fluorescent lamp of Fig.3, what is called two layer application may be chosen in which a first layer on the inner surface of the light transmittable glass is formed as long decay phosphor layer 31 with a second layer 32 being formed as an illuminating fluorescent substance layer. According to this method, 253.7nm mercury rays are used for exciting the illuminating fluorescent substance. Ultraviolet rays which is not used for exciting the illuminating fluorescent substance but transmitted through the illuminating fluorescent substance layer reach the long decay phosphor layer and excite the long decay phosphor. In addition, visible light emitted from the illuminating fluorescent substance layer reach the long decay phosphor layer and is used for exciting long decay phosphor. In this case, the long decay phosphor is excited by both of the ultraviolet rays and the visible light, and the obtained aftergrow lamp is a high brightness degree illuminating lamp, and the obtained aftergrow is also of high brightness degree.

Furthermore, as shown in a sectional view of a fluorescent lamp of Fig. 4, it is possible that an illuminating fluorescent substance layer 3 is formed on the inner surface of a light transmittable glass 2 with a long decay phosphor layer 4 being formed on the outer surface thereof.

As the fluorescent substance included in the abovementioned fluorescent substance layer in the state of being mixed and used with the long decay phosphor, applicable are fluorescent substances usually usable as illuminating fluorescent substance, for example,

(SrCaBaMg)<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu, BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu, Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu, LaPO<sub>4</sub>:Ce, Tb, MgAl<sub>11</sub>O<sub>19</sub>:Ce, Tb, Y<sub>2</sub>O<sub>3</sub>:Eu, Y(PV)O<sub>4</sub>:Eu, 3.5MgO·0.5MgF<sub>2</sub>·GeO<sub>2</sub>:Mn, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>FCl:Sb, Mn, Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>FCl:Sb, Mn, (SrMg)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>:Eu, Sr<sub>2</sub>P<sub>2</sub>O<sub>7</sub>:Eu, CaWO<sub>4</sub>, CaWO<sub>4</sub>:Pb, MgWO<sub>4</sub>, (BaCa)<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu, Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu, Zn<sub>2</sub>SiO<sub>4</sub>:Mn, BaSi<sub>2</sub>O<sub>5</sub>:Pb, SrB<sub>4</sub>O<sub>7</sub>:Eu, (CaZn)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>:Tl, and LaPO<sub>4</sub>:Ce.

Red color fluorescent substances which emits light mainly of more than 600nm wavelength are not used for exciting the long decay phosphor. This is because fluorescent substances of such long wavelengths cannot excite the long decay phosphor. However, usual illuminating fluorescent lamp often emit light throughout the visible range, and therefore when such fluorescent lamps are provided with an aftergrow characteristics, red color light is not necessary for the long decay phosphor but is necessary for setting the light color of the fluorescent lamp in a required range. As the fluorescent substance, most preferable is a three wavelength fluorescent mixture consisting of a blue light emitting fluorescent substance having the light emission peak wavelength near 450nm, a green light emitting fluorescent substance having the light emission peak wavelength near 545nm and a red light emitting fluorescent substance having the light emission peak wavelength near 610nm in the respects that this fluorescent mixture can highly excite the long decay phosphors, can emit light in the white color range as an illuminating fluorescent lamp, and can freely change the light color of the fluorescent lamp. As the blue light emitting fluorescent substance, (SrCaBaMg)<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu and BaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub>:Eu can be preferably used. As the green light emitting fluorescent substance, LaPO<sub>4</sub>:Ce, Tb, and MgAl<sub>11</sub>O<sub>19</sub>:Ce, Tb fluorescent substances can be preferably used. And as the red light emitting fluorescent substance, Y<sub>2</sub>O<sub>3</sub>:Eu can be preferably used.

The mixing ratio of the long decay phosphor constituting the

fluorescent substance layer and the fluorescent substance for the fluorescent lamp which is mixed therewith can be freely changed according to the use purpose of the lamp. For example, when the use purpose as an illuminating fluorescent lamp has priority and thus the luminous flux of the lamp is most important, the proportion of the fluorescent substance for the fluorescent lamp is increased. On the contrary, when bright and long aftergrow is required, it can be realized by increasing the proportion of the long decay phosphor.

Further, for manufacturing an aftergrow fluorescent lamp, a usual method for manufacturing fluorescent lamps can be applied as it is. For example, a long decay phosphor, a fluorescent substance which is put together with the long decay phosphor for exciting the same, and a binding agent such as alumina, calcium pyrophosphate or calcium barium borate are added to a nitro cellulose/butyl acetate solution, mixed and suspended to prepare a fluorescent substance coating suspension. The obtained fluorescent substance coating suspension is run on the inner surface of the glass tube of the fluorescent lamp, and thereafter dried by blowing hot air. Then, the fluorescent lamp can be completed according to the usual manufacturing steps including baking, air discharging, filament fitting, base attachment and the like.

At the time of coating the suspension on the inner surface of the tube, it is possible to make firstly a protecting layer of e.g. alumina and then form a fluorescent substance layer thereon. By using such a method, the light emitting qualities of the fluorescent lamp such as luminous flux and the luminous flux maintenance factor can be further improved.

As the raw material of the long decay phosphor used for carrying out the present invention, metal oxides such as  $\text{SrO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$ , or compounds which can easily become oxides by firing at a high temperature such as  $\text{SrCO}_3$ . As such compounds, there are nitrates, oxalates and

hydroxide, in addition to carbonates. Since the light emitting qualities depend on the purity of the material, the purity of these raw materials must be more than 99.9%, and preferably are more than 99.99%.

By adding halogen element as a flux to the long decay phosphor and heating the mixture, extraordinary particle growth of the long decay phosphor can be controlled and thereby crystal growth thereof can be also controlled. This is because the halogen element react with aluminium, alkaline earth metals and rare earth metals included in the long decay phosphor, and the long decay phosphor with the reactant being mainly on the particle surfaces of the fluorescent substance is reacted, so that the particles of the long decay phosphor can be uniformly formed. As a result, the particle shape of the long decay phosphor as well as the dispersibility thereof can be improved.

As the halogen compound added as a flux to the raw materials of long decay phosphor at the time of heating, ammonium salts of halogen elements, halogenide of alkaline earth elements, aluminium halogenide or the like are used singly or as a mixture. Almost whole of the added halogen element are contained in the resulted composition of the long decay phosphor. Therefore, by adding such an amount of the halogen element as desired to be contained in the resulted long decay phosphor to the raw material and burning the mixture, the halogen content of the long decay phosphor can be controlled.

The halogen content  $\alpha$  of the long decay phosphor depends upon the composition of the long decay phosphor. It depends especially upon the mol value  $n$  of boroaluminate in the composition formula of the long decay phosphor according to the present invention. With the value  $n$  being in the range more than 0.5 and less than 1.5, the emitted light of the long decay phosphor is green when the alkaline earth metal is Sr, and is blue when it is Ca, and the range of  $\alpha$  is preferably more than 0.003 and less

than 0.2, and more preferably is less than 0.05 and more than 0.12. Further, with the value  $n$  being in the range more than 1.5 and less than 3.0, the emitted light is blue green, and the range of  $\alpha$  is preferably more than 0.004 and less than 0.25 and more preferably is less than 0.08 and more than 0.15. Further, the value  $\alpha/n$  is preferably more than 0.001 and less than 0.4 and most preferably near 0.07.

By putting boron into the composition of the long decay phosphor, the resultant boroaluminate can improve the crystalline characteristics, and can stabilize the luminescence center and the light trapping center, so that the brightness degree of the afterglow can be effectively increased.

In order to put boron into the composition of the long decay phosphor, it is effective to add a compound containing boron as a flux to the raw material and heat the same. As such a flux, boracic acid or borates of alkaline earth elements can be used and especially, boric acid is preferable. Almost the whole amount of the added boron is contained in the composition of the long decay phosphor.

In adding boron, the value  $m$  of the boron substituting aluminum is preferably in the range more than 0.0001 and less than 0.5, and more preferably is near 0.05.

By adding a specified amounts of boric acid and phosphoric acid to the raw material, almost the whole amount of the added boric acid together with alumina produces mixed crystal and it is incorporated into the composition of the long decay phosphor, so that heat resistance of the long decay phosphor can be improved. Excessive boric acid, together with phosphoric acid compounds and divalent metals produces mixed crystal, which serves for preventing fusion between particles. This mixed crystal, being insoluble in water, covers particle surfaces of the long decay phosphor and therefore has water resistance. In order to put

phosphoric acid into the composition of the long decay phosphor, preferably phosphoric acid, phosphoric anhydride, ammonium phosphate, phosphates of alkaline earth metals and the like are used. Almost the whole amount of phosphoric acid is contained in the resultant composition of the fluorescent substance. The phosphoric compound is added in such an amount that the phosphoric acid concentration  $k$  becomes preferably more than 0.001 and less than 0.2, more preferably more than 0.01 and less than 0.1, and most preferably more than 0.03 and less than 0.05.

The material comprising these components and the flux mixed together is subject to a primary heating in the atmosphere at a temperature higher than 1200°C and lower than 1600°C for a few hours, and thereafter subject to a secondary heating in a weak reduction atmosphere at a temperature higher than 1200°C and lower than 1600°C. By grinding and sieving the resultant formed substance, a long decay phosphor according to the present invention can be obtained. The mixing ratio of the components in the material for the purpose of obtaining the objective long decay phosphor composition is substantially equal to the theoretical ratio.

An activator and a coactivator put into the long decay phosphor relate to the fluorescent color and the aftergrow brightness degree, and the concentration ranges of the activator and the coactivator agent are important for practical use. Therefore these concentrations are selected in the following ranges.

The concentration  $p$  of an activator Eu put into the long decay phosphor is preferably in a range higher than 0.001 and lower than 0.06.

As the coactivator, at least one selected from a group consisting Mn, Dy, Tm, Lu, Nb, Yb, Zr, Er, Pr, Ho and Nd can used, but preferably two selected therefrom are used. The two elements can be regarded as a first and a second coactivator. As the first coactivator, mainly each of Dy, Nd, Pr, Ho and Er can be used. Especially when the divalent metal M is Sr,

each of Dy, Pr, Tm, Ho and Er is effective for improving the aftergrow brightness, and in this case the emitted light color is in the range from green to blue green. When the divalent metal M is mainly Ca, each of Nd and Tm is effective for improving the aftergrow brightness, and in this case the emitted light color is in the range from blue to purplish blue. When the divalent metal M is mainly Ca, the combination of the first coactivator Nd and the second coactivator Mn can provide a highly efficient aftergrow in the range of white color.

When Dy is selected as the first coactivator, the optimum range of the Dy concentration q for obtaining excellent light qualities is from 0.0005 to 0.03.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Mn is preferably from 0.0001 to 0.06, and more preferably from 0.0005 to 0.02.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Tm is preferably from 0.0003 to 0.02, and more preferably from 0.0004 to 0.01.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Lu is preferably from 0.0001 to 0.06, and more preferably from 0.0004 to 0.04.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Nb is preferably from 0.0001 to 0.08, and preferably from 0.0003 to 0.04.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Yb is preferably from 0.0002 to 0.04, and more preferably from 0.0003 to 0.01.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Zr is preferably from 0.002 to 0.70.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Er is preferably from 0.0001 to 0.03, and more preferably from 0.0005 to 0.02.

When Dy is selected as the first coactivator, the range of the concentration q of the second coactivator Pr is preferably from 0.0001 to 0.04, and more preferably from 0.0005 to 0.03.

When Nd is selected as the first coactivator, the optimum range of the concentration q of Nd is from 0.0005 to 0.03. In this case, the second coactivator may not necessarily be used at the same time.

When Nd is selected as the first coactivator, the range of the concentration q of the second coactivator Tm is preferably from 0.0001 to 0.06, and more preferably from 0.0005 to 0.02.

When Nd is selected as the first coactivator, the range of the concentration q of the second coactivator Pr is preferably from 0.0001 to 0.06, and more preferably from 0.0005 to 0.02.

When Nd selected as the first coactivator, the range of the concentration q of second coactivator Ho is preferably from 0.0001, to 0.06 and more preferably from 0.0005 to 0.02.

When Nd is selected as the first coactivator, the range of the concentration q of the second coactivator Dy is preferably from 0.0001 to 0.06, and more preferably from 0.0005 to 0.02.

As a long decay phosphor having comparatively long time aftergrow, ZnS:Cu fluorescent substance has been conventionally known. However, if an aftergrow lamp is manufactured with this long decay phosphor, the aftergrow luminous flux is extremely low and such a brightness as being usable for illuminating cannot be obtained. This is because ZnS:Cu fluorescent substance is optically decomposed by ultraviolet rays, so that zinc metal in colloid state is deposited on the crystal surface of the fluorescent substance and it changes the outer color of the

fluorescent substance to black. As a result, the aftergrow brightness of the fluorescent substance is remarkably lowered. Furthermore, at the baking step for burning the organic binder after the fluorescent substance applying step, ZnS : Cu fluorescent substance is oxidized and cease to emit light. From such fundamental reasons, such a kind of fluorescent substance cannot be applied to a fluorescent lamp.

Unlike the conventional fluorescent substance, the abovementioned boroaluminate long decay phosphor used according to the present invention is not optically decomposed by ultraviolet rays. Besides, mercury adsorption by the fluorescent substance which is one of the main causes of deterioration of a fluorescent lamp at the time of being on, as well as deterioration of the fluorescent substance by ion bombardment of  $\text{Ar}^+$ ,  $\text{Hg}^+$  and the like emitted from the positive column of the fluorescent lamp hardly occur.

This boroaluminate long decay phosphor principally emits bright aftergrow by the effect of divalent Eu of an activator. The divalent Eu effects absorption in a wide range from visible light to ultraviolet rays, and like natural light, the boroaluminate long decay phosphor is excited in a wide wavelength range to highly efficiently emit light (fluorescent light). Further, by doping to the long decay phosphor composition at least one selected from a group consisting of Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, aftergrow phenomenon occurs.

According to the present invention, boroaluminate fluorescent substance is used, which, because of containing boron, can improve the crystalline characteristics of the aluminate and stabilize the luminescence center and the trapping center, so that improved aftergrow time and aftergrow brightness be obtained.

When the ratio of the whole mol number of the oxides of the divalent metals, the activator and the coactivators and the whole mol number of

the alumina and the boric acid is 1:1, namely  $n=1$ , it is proved through x-ray diffraction of the fluorescent substance that the crystalline structure is a monoclinic system of  $\text{SrAl}_2\text{O}_4$  type and the fluorescent substance emits green light having the light emission peak wavelength 520nm.

When the abovementioned components and additives are mixed and heated with the mol number ratio being 1:2, namely  $n=2$ , with a low concentration about 1 mol% of boron substitution,  $\text{SrAl}_4\text{O}_2$  which is the structure ought to be produced from the composition of the material is produced.

However, with a higher concentration of boron substitution, a mixture of  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  structure and  $\text{SrAl}_{12}\text{O}_{10}$  structure are produced. Especially important one of these crystalline structures is  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  structure and it belongs to rhombic system. Since the long decay phosphor contains a predetermined amount of boron, the crystalline structure thereof is changed and the aftergrow characteristics are improved. Especially when  $n$  is about 1.75, blue green light having the light emission peak wavelength 490nm is most strong, and as a result of X-ray diffraction, a high purity of a long decay phosphor having  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  structure which is expected from the amounts of the composition of the material can be obtained. This long decay phosphor having  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  structure is obtained in the range  $1.5 \leq n \leq 3.0$ , and especially, it can be obtained as the main product in the range  $1.7 \leq n \leq 2.1$ .

This long decay phosphor having crystalline structure of rhombic system is more excellent in heat resistance than the fluorescent substance having crystalline structure of monoclinic system obtained in the range  $0.5 \leq n \leq 1.5$ . Therefore, this long decay phosphor can advantageously provide high aftergrow characteristics when it is used in a lamp such as a fluorescent lamp in which the fluorescent layer is

subject to baking at a high temperature in the manufacturing process. The heat resistance of this boroaluminate long decay phosphor is lowered as the boric acid content thereof increases. And, the formed product of this long decay phosphor is solid and therefore is hard to be treated in the following step of grinding, sieving and the like. However, by adding phosphoric acid compound to the composition raw material and the same, heat resistance and water resistance can be improved.

The most part of the added phosphoric acid produces mixed crystal together with alumina and incorporated into the long decay phosphor composition. However, it is regarded that the excessive phosphoric acid produces mixed crystal together with phosphoric compound and divalent metal and serves for preventing fusion between the long decay phosphor particles, thereby contributing to the improvement of the heat resistance. Further, since this mixed crystal, being insoluble in water, covers the particle surfaces of the long decay phosphor, it improves the water resistance of the long decay phosphor.

#### EXAMPLE 1

In this example, a case will be described in which green color light emitting long decay phosphor  $(\text{Sr}_{0.95}\text{Eu}_{0.03}\text{Dy}_{0.015})_0.91(\text{Al}_{0.95}\text{Ba}_{0.05})_2\text{O}_3\text{O} \cdot 0.03\text{P}_2\text{O}_5 \cdot 0.1\text{F}$  is excited and made to emit light by a three wavelength mixed fluorescent substance, and especially in which these fluorescent substance are fully mixed in the fluorescent layer of a fluorescent lamp.

As the raw material of a long decay phosphor, 140.98g (0.955 mol) of  $\text{SrCO}_3$ , 88.14g (0.865 mol) of  $\text{Al}_2\text{O}_3$ , 5.28g (0.015 mol) of  $\text{Eu}_2\text{O}_3$ , 2.80g (0.0075 mol) of  $\text{Dy}_2\text{O}_3$ , 5.63g (0.091 mol) of  $\text{H}_3\text{BO}_3$ , 7.92g (0.060 mol) of  $(\text{NH}_4)_2\text{HPO}_4$  and 3.70g (0.10 mol) of  $\text{NH}_4\text{F}$  were put into a ceramic pot. Alumina balls as a mixing medium were added thereto, and the mixture were blended by a

roller for 2 hours and a mixed raw material before long decay phosphor formed (hereinafter referred to as material raw powder) was obtained. Then, the raw material powder was put into a boat-shaped crucible, and heated in a tubular furnace in the atmosphere at 1300 °C for 2 hours. Then, it was further heated for several hours with a flow of mixed gas consisting of nitrogen and hydrogen, and a formed product of the long decay phosphor was obtained. Thereafter, the burned product was grinded and sieved through a 200 mesh screen, and a long decay phosphor is obtained. This long decay phosphor shows emission of green light having light emission peak wavelength 515nm and a high spectral luminous efficacy.

The obtained long decay phosphor and a three wavelength mixed fluorescent substance obtained by mixing 32% of  $(\text{SrCaBaMg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}$  blue light emitting fluorescent substance having the light emission peak wavelength 453nm, 18% of  $\text{LaPO}_4:\text{Ce}$ , Tb green light emitting fluorescent substance having the light emission peak wavelength 544nm and 50% of  $\text{Y}_2\text{O}_3:\text{Eu}$  red light emitting fluorescent substance having the light emission peak wavelength 611nm were fully mixed in the ratio of 1:4. 20g of the mixed fluorescent substance and 15g of nitrocellulose/butyl binder were fully mixed in a ceramic pot to prepare fluorescent substance coating slurry. This slurry was flowed into a glass tube to coat on the inner surface of the glass tube and dried with heated air, and thereby a fluorescent substance coated bulb was obtained. Then, the long decay phosphor applied bulb was subject to baking at 580 °C for 15 minutes, whereby a fluorescent layer was formed. The amount of the fluorescent substance coated on one fluorescent lamp was 5.0g. Thereafter, steps of gas discharging, filament fitting and base attachment were carried out according to the conventional method, and a FL40SS fluorescent lamp was manufactured. Data of the obtained aftergrow fluorescent lamp are shown

in Table 1.

#### EXAMPLE 2

Two layer application will be now described in which  $(\text{Sr}_{0.95}\text{Eu}_{0.05}\text{Dy}_{0.015})_0.91(\text{Al}_{0.95}\text{B}_{0.05})_2\text{O}_3 \cdot 0.03\text{P}_2\text{O}_5 \cdot 0.1$  long decay phosphor obtained in EXAMPLE 1 is coated as a first layer on a fluorescent lamp and the three wavelength mixed fluorescent substance is coated as a second layer batnce thereon.

12g of the fluorescent substance and 15g nitrocellulose /butyl acetate binder were sufficiently mixed in a ceramic pot to prepare fluorescent substance coating slurry. This slurry is flowed into a glass tube to be coated on the inner surface of the glass tube and dried with heated air. The amount of the long decay phosphor thus formed as the first layer was 3g. Then, 50g of polyethylene oxide water solution was added to 30g of a three wavelength mixed fluorescent substance obtained by mixing 34.7% of  $(\text{SrCaBaMg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}$  blue light emitting fluorescent substance, 20.1 % of  $\text{LaPO}_4:\text{Ce}$ , Tb green light emitting fluorescent substance and 45.2 % of  $\text{Y}_2\text{O}_3:\text{Eu}$  red light emitting fluorescent substance, and the mixture was sufficiently mixed in a ceramic pot to prepare fluorescent substance coating slurry. This slurry was flowed into the glass tube to be applied on the inner surface of the tube and dried with heated air. The amount of the three wavelength mixed fluorescent substance thus formed as the second layer was 3g. Then, the two layer coated bulb was subject to baking, at 580 °C for 15 minutes whereby a fluorescent substance layer was formed. Thereafter, step of gas discharging, filament fitting and base attachment were carried out according to the conventional method, and a FL40SS fluorescent lamp was obtained. Data of the fluorescent lamp are shown in Table 1.

### EXAMPLE 3

In this example,

$(\text{Ca}_{0.55}\text{Eu}_{0.015}\text{Nd}_{0.03})_2\text{O}_3 \cdot 0.97(\text{Al}_{0.95}\text{Ba}_{0.05})_2\text{O}_3 \cdot 0.03\text{P}_2\text{O}_5 \cdot 0.1\text{F}$  blue light emitting long decay phosphor is excited to emit light by a three wavelength mixed fluorescent substance, especially in a case in which these fluorescent substance are fully mixed in a fluorescent layer of a fluorescent lamp.

A long decay phosphor was prepared by the same method as described in EXAMPLE 1 except that as the material of the fluorescent substance, 95.59g (0.955 mol) of  $\text{CaCO}_3$ , 94.01g (0.922 mol) of  $\text{Al}_2\text{O}_3$ , 2.64g (0.0075 mol) of  $\text{Eu}_2\text{O}_3$ , 5.05g (0.015 mol) of  $\text{Nd}_2\text{O}_3$ , 6.00g (0.097 mol) of  $\text{H}_3\text{BO}_3$ , 7.92g (0.060 mol) of  $(\text{NH}_4)_2\text{HPO}_4$  and 3.7g (0.1 mol) of  $\text{NH}_4\text{F}$  are used. This fluorescent substance showed blue light emission having the light emission peak wavelength 440nm. The obtained long decay phosphor and a three wavelength mixed fluorescent substance obtained by mixing 17% of  $(\text{SrCaBaMg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}$  blue light emitting fluorescent substance, 27% of  $\text{La PO}_4:\text{Ce}$ ,  $\text{Tb}$  green light emitting fluorescent substance and 46% of  $\text{Y}_2\text{O}_3:\text{Eu}$  red light emitting fluorescent substance are sufficiently mixed in the ratio of 1:4, and a FL40SS fluorescent lamp is obtained by the same method as described in EXAMPLE 1. Data of the obtained fluorescent lamp are shown in Table 1.

### EXAMPLE 4

In this example,

$(\text{Sr}_{0.70}\text{Eu}_{0.01}\text{Dy}_{0.02})_2\text{O} \cdot 1.78(\text{Al}_{0.99}\text{Ba}_{0.014})_2\text{O}_3 \cdot 0.03\text{P}_2\text{O}_5 \cdot 0.1\text{F}$  blue green light emitting long decay phosphor is excited to emit light by a three wavelength mixed fluorescent substance especially in a case in which these fluorescent substances are fully mixed in a fluorescent layer of a fluorescent lamp.

As the raw materials of the long decay phosphor, 572.8g (3.88 mol) of SrCO<sub>3</sub>, 713.72g (7.0 mol) of Al<sub>2</sub>O<sub>3</sub>, 7.04g (0.02 mol) of Eu<sub>2</sub>O<sub>3</sub>, 14.92g (0.04 mol) of Dy<sub>2</sub>O<sub>3</sub>, 12.4g(0.2 mol) of H<sub>3</sub>BO<sub>3</sub>, 7.92g (0.06 mol) of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and 3.7g (0.1 mol) of NH<sub>4</sub>F were used. Similar to EXAMPLE 1, these materials were put into a ceramic pot, added with alumina balls as a mixing medium and mixed by a roller for 2 hours, so that a raw material powder was obtained. The raw material powder was put into a boat-shaped crucible, and heated in a tubular furnace in the atmosphere at 1300°C for 2 hours. Then, it was further burned for several hours with a flow of mixed gas consisting of nitrogen and hydrogen, and a burned product of the fluorescent substance was obtained. Then the burned product was grinded and sieving through a 200 mesh screen, and a long decay phosphor is prepared. The long decay phosphor shows emission of blue green light having light emission peak wavelength 490nm.

The obtained long decay phosphor and three wavelength mixed fluorescent substance obtained by mixing 22.3% of (SrCaBaMg)<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu blue light emitting fluorescent substance, 33.3% of LaPO<sub>4</sub>:Ce, Tb green light emitting fluorescent substance and 44.4% of Y<sub>2</sub>O<sub>3</sub>:Eu red light emitting fluorescent substances were sufficiently mixed in the ratio of 1:3. 20g of this mixed fluorescent substance and 15g of nitrocellulose/butyl acetate binder were sufficiently mixed in a ceramic pot to prepare fluorescent substance coating slurry. This slurry was flowed into a glass tube to be coated on the inner surface of the glass tube and dried with heated air, and thereby a fluorescent substance bulb was obtained. Then, the fluorescent substance applied bulb was subject to baking at 580°C for 15 minutes, whereby a fluorescent layer was formed. The amount of the fluorescent substance coated on one fluorescent lamp was 5.0g. Thereafter, steps of gas discharging, filament fitting and base attachment were carried out according to the conventional method and a

FL40SS aftergrow fluorescent lamp was obtained. Date of the aftergrow fluorescent lamp are shown in table 1.

#### EXAMPLE 5

Two layer coating will be now described in which  $(\text{Sr}_{0.970}\text{Eu}_{0.01}\text{Dy}_{0.02}) \cdot 1.78(\text{Al}_{0.988}\text{Ba}_{0.014})_2\text{O}_3 \cdot 0.03\text{P}_2\text{O}_5 \cdot 01\text{F}$  long decay phosphor prepared in EXAMPLE 4 is coated as a first layer on a fluorescent lamp and a three wavelength mixed fluorescent substance is coated as a second layer thereon.

12g of the long decay phosphor and 15g of nitrocellulose/butyl acetate binder were sufficiently mixed in a ceramic pot to prepare fluorescent substance coating slurry. This slurry is flowed into a glass tube to be coated on the inner surface of the glass tube and dried with heated air. The amount of the long decay phosphor thus coated as the first layer was 3g. Then, 50g of polyethylene oxide water solution was added to 30g of a three wavelength mixed fluorescent substance of obtained by mixing 20.6 % of  $(\text{SrCaBaMg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}$  blue light emitting fluorescent substance, 34.2 % of  $\text{LaPO}_4:\text{Ce}$ , Tb green light emitting fluorescent substance and 45.2 % of  $\text{Y}_2\text{O}_3:\text{Eu}$  red light emitting fluorescent substance, and the mixture was sufficiently mixed in a ceramic pot to prepare fluorescent substance coating slurry. This slurry was flowed into the glass tube to be coated on the inner surface of the glass tube and dried with heated air. The amount of the three wavelength mixed fluorescent substance thus coated as the second layer was 4g. Then, the two layer coated bulb was subject to baking at 580 °C for 15 minutes, whereby a fluorescent layer was formed. Thereafter, steps of gas discharging, filament fitting and base attachment were carried out according to the conventional method, and a FL40SS fluorescent lamp was obtained. Data of the obtained fluorescent lamp are shown in Table 1.

Table 1

EXAMPLE	value X	value Y	aftergrow luminous flux 1m
EXAMPLE1	0.346	0.364	3545
EXAMPLE2	0.347	0.360	3350
EXAMPLE3	0.340	0.357	3271
EXAMPLE4	0.347	0.365	3557
EXAMPLE5	0.342	0.352	3402

Aftergrow luminous flux measured immediately after putting off the light

As shown in this table, the fluorescent lamps made by way of experiment in the abovementioned EXAMPLES 1 to 5 had luminous flux more than 3200 lm As to the aftergrow light flux 5 minutes after putting off the light, that of the fluorescent lamp of Example 4 was 335 lm while that of the fluorescent lamp of Example 5 was 312 lm, which were both excellent values.

Since a long decay phosphor coated on a fluorescent lamp is baked in the process of manufacturing the fluorescent lamp, it is important that the long decay phosphor has excellent heat resistance. A long decay phosphor having excellent heat resistance shows excellent light emitting qualities in finished goods of fluorescent lamps. Further, the long decay phosphor is required to have excellent water resistance in accordance with its use purpose. In order to test the heat resistance and the water

resistance of long decay phosphors, the long decay phosphors having the following compositions of EXAMPLES 6 to 22 were made by way of experiments. These long decay phosphors are made by the same method as used in EXAMPLE 1 except that the materials of the fluorescent substances were changed. The composition formulas of the long decay phosphor are shown in Table 2, while the phosphorescent brightness degrees thereof are shown in Table 3.

Table 2

	composition formula
6	(Sr <sub>0.955</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> ) <sub>0.1.75</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
7	(Sr <sub>0.95</sub> Eu <sub>0.035</sub> Dy <sub>0.015</sub> ) <sub>0.1.75</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
8	(Sr <sub>0.95</sub> Eu <sub>0.035</sub> Dy <sub>0.015</sub> Pr <sub>0.003</sub> ) <sub>0.1.75</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
9	(Sr <sub>0.95</sub> Eu <sub>0.035</sub> Dy <sub>0.015</sub> Ho <sub>0.003</sub> ) <sub>0.1.75</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
10	(Sr <sub>0.95</sub> Eu <sub>0.035</sub> Dy <sub>0.015</sub> Tm <sub>0.003</sub> ) <sub>0.1.75</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
11	(Sr <sub>0.95</sub> Eu <sub>0.035</sub> Dy <sub>0.015</sub> ) <sub>0.1.80</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
12	(Sr <sub>0.95</sub> Eu <sub>0.035</sub> Ho <sub>0.015</sub> ) <sub>0.1.75</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
13	(Sr <sub>0.95</sub> Eu <sub>0.035</sub> Pr <sub>0.015</sub> ) <sub>0.1.75</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
14	(Sr <sub>0.955</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> ) <sub>0.0.91</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
15	(Sr <sub>0.955</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> ) <sub>0.0.91</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub>
16	(Sr <sub>0.952</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> Tm <sub>0.003</sub> ) <sub>0.0.91</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
17	(Sr <sub>0.952</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> Tm <sub>0.003</sub> ) <sub>0.0.91</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub>
18	(Sr <sub>0.952</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> Mn <sub>0.003</sub> ) <sub>0.0.91</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.03P <sub>2</sub> O <sub>5</sub>
19	(Sr <sub>0.952</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> Mn <sub>0.003</sub> ) <sub>0.0.91</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub>
20	(Sr <sub>0.955</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> ) <sub>0.0.97</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.01P <sub>2</sub> O <sub>5</sub>
21	(Sr <sub>0.955</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> ) <sub>0.0.85</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.05P <sub>2</sub> O <sub>5</sub>
22	(Sr <sub>0.955</sub> Eu <sub>0.03</sub> Dy <sub>0.015</sub> ) <sub>0.0.76</sub> (Al <sub>0.95</sub> B <sub>0.05</sub> ) <sub>2</sub> O <sub>3</sub> ·0.08P <sub>2</sub> O <sub>5</sub>

Table 3

	value X/ value Y	phosphorescent brightness % (after 20 min.)	heat resistance (maintenance rate %)	water resistance (maintenance rate %)
6	0.146/0.357	85.2	91.2	96.8
7	0.146/0.356	80.5	92.3	97.0
8	0.148/0.354	83.7	98.5	95.3
9	0.146/0.355	85.9	90.7	96.5
10	0.145/0.355	90.7	92.5	95.7
11	0.146/0.356	85.8	92.8	97.0
12	0.146/0.355	90.3	95.3	94.8
13	0.145/0.356	91.2	95.8	92.5
14	0.248/0.561	98	76.6	49.1
15	0.267/0.586	61	25.1	0
16	0.249/0.573	122	69.3	42.9
17	0.269/0.585	100	17.9	0
18	0.251/0.574	72	49.7	27.4
19	0.265/0.587	54	21.5	0
20	0.264/0.583	77	42.9	37.5
21	0.245/0.550	115	62.8	57.4
22	0.254/0.561	81	64.0	48.7

The heat resistances and the water resistances shown in Table 3 were calculated as follows. 10g of each long decay phosphor was put into a quartz crucible, and was subject to oxidization in a muffle furnace at 600 °C for 30 minutes. The phosphorescent brightness of the product was measured. Then, the percentage of this phosphorescent brightness to the phosphorescent brightness of the long decay phosphor measured before being heated was calculated as the maintenance rate.

The water resistances shown in Table 3 were calculated as follows. 10g of each long decay phosphor and 200g of pure water were put into a plastic container, and rotated by a roller at a speed of 30rpm for 72 hours. Then, the solid substance was separated from the liquid and dried. Thereafter, the phosphorescent brightness of the long decay phosphor was measured. Then the percentage of this phosphorescent brightness to the phosphorescent brightness of the long decay phosphor measured before contacting with water was calculated as the maintenance rate.

As shown in these Tables, the long decay phosphors consisting of boroaluminate fluorescent substances of EXAMPLES 6 to 13 having rhombic system crystalline structure with the value in the composition being more than 1.5 as the main component exhibited remarkably excellent heat resistance and water resistance in comparison with the boroaluminate fluorescent substances of EXAMPLES 14 to 22 having monoclinic system crystalline structure with the value n being near 1. Further, the boroaluminate fluorescent substances which, being added with a phosphoric acid compound at the time of burning contained phosphoric acid in the composition exhibited more excellent water resistance in comparison with the boroaluminate fluorescent substances of EXAMPLES 15, 17 and 19 which did not contain any phosphoric acid compound.

A fluorescent substance coated on the inner surface of a fluorescent lamp is subject to baking at about 600 °C in the process of manufacturing

the lamp. A long decay phosphor having high heat resistance is especially useful for application to a fluorescent lamp and the like which are heated to a high temperature in the manufacturing process. Further, an aftergrow fluorescent lamp having excellent water resistance is suitable for application to lamps which are put in direct contact with the outer air.

#### REFERENCE EXAMPLE 1

ZnS:Cu long decay phosphor selected as a long decay phosphor and a three wavelength mixed fluorescent substance obtained by mixing 34.1% of  $(\text{SrCaBaMg}_5(\text{PO}_4)_3\text{Cl})_{\text{Eu}}$  blue light emitting fluorescent substance, 16.8% of  $\text{LaPO}_4:\text{Ce}$ , Tb green light emitting fluorescent substance and 49.1% of  $\text{Y}_2\text{O}_3:\text{Eu}$  red light emitting fluorescent substance were sufficiently mixed in the ratio of 1:3. And by the same method as used in EXAMPLE 1, a FL40SS fluorescent lamp was manufactured. The obtained fluorescent lamp was wholly blackish and had remarkably low lamp light flux. Therefore, this fluorescent lamp was unmarketable.

#### REFERENCE EXAMPLE 2

Two layer application will be now described in which ZnS:Cu fluorescent substance selected similarly to REFERENCE EXAMPLE 1 is applied as a first layer on the inner surface of a fluorescent lamp, while a three wavelength mixed fluorescent substance is coated thereon as a second layer. 30g of ZnS:Cu fluorescent substance and 15g of nitrocellulose/butyl acetate binder were sufficiently mixed in a ceramic pot to prepare fluorescent substance application slurry. This slurry is flowed into a glass tube to be coated on the inner surface of the glass tube and dried with heated air. The amount of the long decay phosphor thus applied as the first layer was 3g.

Then, 50g of polyethylene oxide water solution was added to a three wavelength mixed fluorescent substance obtained by mixing 30.2% of  $(\text{SrCaBaMg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}$  blue light emitting fluorescent substance, 29.4% of  $\text{LaPO}_4:\text{Ce}$ , Tb green light emitting fluorescent substance and 40.4% of  $\text{Y}_2\text{O}_3:\text{Eu}$  red light emitting fluorescent substance. This mixture was sufficiently mixed in a ceramic pot to prepare fluorescent substance coating slurry. This slurry was flowed into the glass tube to be coated on the inner surface of the glass tube and dried with heated air. The amount of the three wavelength mixed fluorescent substance thus coated as the second layer was 3g.

Thereafter, steps of gas discharging, filament fitting and base attachment were carried out according to the conventional method, and a FL40SS fluorescent lamp was manufactured. The obtained fluorescent lamp was wholly blackish and had remarkably low lamp luminous flux. Therefore, this fluorescent lamp was unmarketable.

As this invention may be embodied in several forms without departing from the spirit of essential characteristics thereof, the present embodiment is therefore illustrative and not restrictive, since the scope of the invention is defined by the appended claims rather than by the description preceding them, and all changes that fall within meets and bounds of claims, or equivalence of such meets and bounds thereof are thereof intended to be embraced by the claims.

**What is claimed is :**

1. An aftergrow lamp comprising

a light emitting section for converting electric energy to optical energy, and

a fluorescent layer which is excited to emit light by the light emitting section, and contains a long decay phosphor represented by the general formula



Whererin the values of p, q, n, m, k,  $\alpha$  and  $\alpha/n$  are in the ranges

$$0.0001 \leq p \leq 0.5$$

$$0.0001 \leq q \leq 0.5$$

$$0.5 \leq n \leq 3.0$$

$$0 \leq m \leq 0.5$$

$$0 \leq k \leq 0.2$$

$$0 \leq \alpha \leq 0.5$$

$$0 \leq \alpha/n \leq 0.4 \text{ and}$$

M is at least one selected from a group of divalent metals consisting of Mg, Ca, Sr, Ba and Zn;

Q is a coactivator and at least one selected from a group consisting of Mn, Zr, Nb, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; and

X is at least one selected from a group of halogen elements consisting of F, Cl, Br and I.

2. An aftergrow lamp as claimed in claim 1, in which the long decay phosphor contained in the fluorescent layer is represented by the general formula



Wherein the value of p, q, n, m, k,  $\alpha$ ,  $\alpha/n$ , are in the ranges

$0.0001 \leq p \leq 0.5$

$0.0001 \leq q \leq 0.5$

$0.5 \leq n < 1.5$

$0.0001 \leq m \leq 0.5$

$0 \leq k \leq 0.2$

$0 \leq \alpha \leq 0.5$

$0 \leq \alpha/n \leq 0.4$  and

more than 70% of M is Sr.

3. An aftergrow lamp as claimed in claim 1, in which the long decay phosphor contained in the fluorescent layer is represented by the general formula



Wherein the values of p, q, n, m, k,  $\alpha$  and  $\alpha/n$  are in the ranges

$0.0001 \leq p \leq 0.5$

$0.0001 \leq q \leq 0.5$

$0.5 \leq n < 1.5$

$0.0001 \leq m \leq 0.5$

$0 \leq k \leq 0.2$

$0 \leq \alpha \leq 0.5$

$0 \leq \alpha/n \leq 0.4$  and

more than 70 mol% of M is Ca.

4. An aftergrow lamp as claimed in claim 1, in which the long decay phosphor contained in the fluorescent layer is represented by the following general formula, and the main component of the crystalline structure of the long decay phosphor is prismatic system



Wherein the values of p, q, n, m, k,  $\alpha$  and  $\alpha/n$  are in the ranges

$0.0001 \leq p \leq 0.5$

$0.0001 \leq q \leq 0.5$

$1.5 \leq n \leq 3.0$

$0.0001 \leq m \leq 0.5$

$0 \leq k \leq 0.2$

$0 \leq \alpha \leq 0.5$

$0 \leq \alpha/n \leq 0.4$  and

more than 70 mol% of M is Sr.

5. An aftergrow lamp as claimed in claim 4, in which the long decay phosphor contained the fluorescent layer is represented by the following general formula, and the main component of the crystalline structure of the long decay phosphor is rhombic system



Wherein the values of p, q, n, m, k,  $\alpha$  and  $\alpha/n$  are in the ranges

$0.0001 \leq p \leq 0.5$

$0.0001 \leq q \leq 0.5$

$1.7 \leq n \leq 2.0$

$0.0001 \leq m \leq 0.5$

$0 \leq k \leq 0.2$

$0 \leq \alpha \leq 0.5$

$0 \leq \alpha/n \leq 0.4$  and

more than 70 mol% of M is Sr.

6. An aftergrow lamp as claimed in claim 1, in which the value k representing the phosphoric acid content in the general formula is in the range  $0.001 \leq k \leq 0.2$ .

7. An aftergrow lamp as claimed in claim 1, in which the light emitting

section is a fluorescent lamp, and the fluorescent layer is applied on the inner surface of the fluorescent lamp.

8. An aftergrow lamp as claimed in claim 7, in which the fluorescent layer of the fluorescent lamp includes a fluorescent substance exciting the long decay phosphor and the aftergrow lamp, and the color of the emitted light is in white color range.

9. An aftergrow lamp as claimed in claim 5, in which the light emitting section is a fluorescent lamp, and the fluorescent layer is applied on the inner surface of the fluorescent lamp.

10. An aftergrow lamp as claimed in claim 7, in which the fluorescent layer of the fluorescent lamp includes a fluorescent substance exciting the long decay phosphor and the aftergrow lamp, and the color of the emitted light is in white color range.

11. An aftergrow lamp as claimed in claim 10, in which the fluorescent layer includes at least one of the long decay phosphor and a three wavelength mixed fluorescent substance consisting of a blue light emitting fluorescent substance having light emission peak wavelength near 450nm, a green light emitting fluorescent substance having light emission peak wavelength near 545nm and a red light emitting fluorescent substance having light emission peak wavelength near 610nm.

12. An aftergrow lamp as claimed in claim 7, in which the fluorescent substance of a long decay phosphor layer and an illuminating fluorescent layer, and the illuminating fluorescent layer is provided the long decay phosphor layer.



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Application No: GB 9609495.8  
Claims searched: 1 to 12

Examiner: Colin Sherrington  
Date of search: 21 August 1996

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C4S

Int CI (Ed.6): C09K 11/64

Other: ONLINE: WPI, CLAIMS

**Documents considered to be relevant:**

Category	Identity of document and relevant passage		Relevant to claims
X	GB 1458700	(PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED) -especially page 4, lines 66 to 113; Table 1, page 6, B6; claims 6 to 9	1
X	GB 1483243	(PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED) -especially page 3, lines 2 to 29; Example; claim 5	1
X	GB 2142775 A	(KABUSHIKI KAISHA TOSHIBA) -especially page 1, lines 47 to 55; page 2, lines 2 to 26; Table, Examples 2 & 3; claims 1 to 3	1
X	EP 0418902 A2	(KASEI OPTONIX, LTD.) -whole document, especially Examples 7 to 13, 21 to 27; claims 6 to 8	1
X	EP 0529956 A1	(KABUSHIKI KAISHA TOSHIBA) -whole document	1
X	EP 0622440 A1	(NEMOTO & CO., LTD.) -whole document, especially page 2, lines 1 to 10, lines 41 to 45; page 3, lines 1 to 4; Examples 2 to 11; claims 1 to 4 (& US 5424006)	1 to 5

- X Document indicating lack of novelty or inventive step  
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- A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.



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Application No: GB 9609495.8  
Claims searched: 1 to 12

Examiner: Colin Sherrington  
Date of search: 21 August 1996

Category	Identity of document and relevant passage		Relevant to claims
X	EP 0697453 A1	(MITSUBISHI CHEMICAL CORPORATION et al.) -whole document, especially page 3, lines 25 to 49; page 6, lines 10 to 31; Examples 19 to 23; claims 1 to 5, 9, 10, 14 to 16	1
E.X	EP 0710709 A1	(NEMOTO & CO., LTD.) -whole document, especially page 2, lines 5 to 7, lines 30 to 55; Examples 2 to 11; claims 1 to 7	1 to 5
X	US 4847533	(GENERAL ELECTRIC COMPANY) -whole document, especially column 2, lines 50 to 66; claims 1, 6, 8	1
P,X	Derwent WPI Abstract Accession No. 96-2058814/21 & JP080073845A		1

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